Orientational relaxation and vibrational excitation transfer in methanol–carbon tetrachloride solutions

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Time and polarization resolved ultrafast infrared vibrational spectroscopy of the hydroxyl stretch of methanol dissolved in carbon tetrachloride has been utilized to investigate orientational relaxation and vibrational excitation transfer. The anisotropy decay of the deuterated hydroxyl stretch of methanol-*d* was measured in two solutions: Isotopically mixed 0.8 mol % methanol-*d* 23 mol % methanol-*h* in CCl_4 and isotopically pure methanol-*d* at 26 mol % in CCl_4. The anisotropy decay in the isotopically mixed methanol solution is a biexponential characterized by 1.7 ± 0.7 ps and 17 ± 3 ps time constants, with $40\pm10\%$ of the decay occurring with the slower time constant. The biexponential anisotropy decay has been analyzed with a restricted orientational diffusion model that involves fast orientational diffusion within a cone of semi-angle θ_c, followed by slower, full orientational relaxation. The fast orientational relaxation occurs within a cone semi-angle of $\theta_c = 45°\pm5°$, with a diffusion coefficient of $D_c^{-1}=13\pm5$ ps. The slower anisotropy decay results from the full orientational diffusion and occurs with a diffusion coefficient of $D_\theta^{-1}=100\pm20$ ps. The anisotropy decay for isotopically pure methanol-*d* in CCl_4 is much faster because of vibrational excitation transfer in addition to the orientational relaxation. The excitation transfer has been successfully analyzed as transition dipole–transition dipole mediated transfer using a theory developed for randomly distributed chromophores. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1534580]

I. INTRODUCTION

When a chemical reaction occurs in a dipolar liquid, the reorientation of solvent dipoles represents a prominent event in the response of the solvent to a change in a solute.[1–3] Chemical reactions also produce or consume thermal energy. By supplying or dissipating energy during a chemical reaction, the solvent can influence the yield of chemical reactions. Vibrational excitation transfer provides a mechanism for energy transport away from the reaction site.[4,5]

For associated dipolar liquids, the dynamics of the extended hydrogen bonding networks become the key factor in determining the structural dynamics of the solvent and the rate of intermolecular energy transfer.[6] The present investigation utilizes time and polarization resolved vibrational spectroscopy of the hydroxyl stretch of methanol in carbon tetrachloride solutions to study orientational relaxation and excitation transfer. In previous studies we have utilized time resolved vibrational spectroscopy to monitor the dynamics of hydrogen bond dissociation and reformation following hydroxyl stretch relaxation for a series of alcohols dissolved in CCl_4.[7,8] Those investigations demonstrated that hydrogen bond dissociation follows hydroxyl stretch relaxation sequentially and occurs with two mechanisms; a direct breaking pathway wherein the excited hydroxyl stretch decays into modes that directly lead to the hydrogen bond dissociation and an indirect pathway wherein the dissociation of hydrogen bonds follows vibrational energy flow from the initially

excited molecule to other components of the same oligomer. The current study extends the previous work to address the issues of orientational relaxation and vibrational excitation transfer.

For concentrated methanol in carbon tetrachloride solutions, like those used in the present study, hydrogen bonded oligomers, composed of chains and rings, are the dominant species found in solution.[9–12] The frequency and width of the hydroxyl stretch depends strongly upon the number of hydrogen bonds formed, making the hydroxyl stretch a sensitive probe of hydrogen bonding in solution.[9–13] The infrared absorption spectra of the solutions studied in the present account appear in Fig. 1. Terminal methanol molecules in hydrogen bonded chains have narrower hydroxyl stretch absorptions at significantly higher frequency. The terminal β methanol-*d* that accepts, but does not donate, a hydrogen bond has an absorption peak at ~2690 cm^{-1} with a Lorentzian width of ~20 cm^{-1}.[11,13] The terminal γ methanol-*d* that donates, but does not accept, a hydrogen bond has an absorption peak at ~2600 cm^{-1} with a Gaussian width of ~80 cm^{-1}.[10,11,13] Internal δ methanol-*d* molecules both accept and donate hydrogen bonds and have an absorption peak at ~2490 cm^{-1} with a Gaussian width of ~150 cm^{-1}.[10,11] Internal molecules of chain and ring oligomers participating in two hydrogen bonds represent the dominant configuration in liquid methanol.[14]

This paper presents time dependent anisotropy measurements for high concentrations of methanol dissolved in CCl_4. The experiments involve the excitation of the hydroxyl stretch of deuterated δ methanol at 2500 cm^{-1}. The

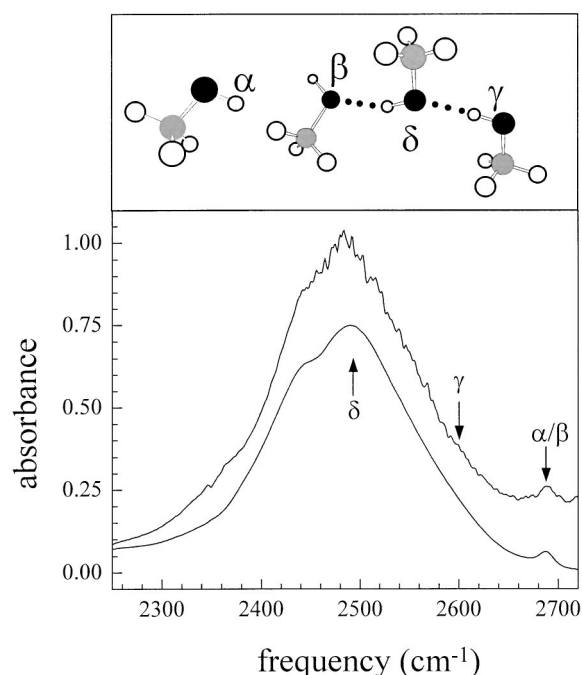[a)]Electronic mail: fayer@fayerlab.stanford.edu

FIG. 1. Steady-state IR spectrum of methanol-d in CCl$_4$ for two types of samples used in the experiments. Concentrations of 26 mol % methanol-d and background subtracted 0.8 mol % methanol-d 23 mol % methanol-h appear from bottom to top. The spectrum contains absorption bands from several species. α refers to isolated monomeric molecules, β to hydroxyl stretches that accept, but do not donate hydrogen bonds, γ to molecules that donate, but do not accept, hydrogen bonds, and δ to molecules that donate and accept hydrogen bonds. The drawing of a monomer and a trimer show the different types of hydroxyl groups with the appropriate labels.

anisotropy decays in two solutions were measured: 26 mol % methanol-d in CCl$_4$ and 0.8 mol % methanol-d in a mixture of 23 mol % methanol-h dissolved in CCl$_4$. These should be viewed as roughly equivalent methanol concentrations for the work described in this paper. In the isotopically mixed methanol solution, the large distance between methanol-d molecules results in a negligible rate of excitation transfer.[15,16] Therefore, the dynamics of orientational relaxation can be measured without complications produced by excitation transfer. The anisotropy decay in the isotopically mixed solution exhibits a biexponential relaxation. Dielectric relaxation[17] measurements of orientational relaxation in methanol–CCl$_4$ solutions, as well as terahertz spectroscopy[18] and dielectric relaxation[19] measurements in liquid methanol, have multiexponential decays, which have been analyzed with a multiple Debye model of orientational relaxation. While providing an effective parameterization of the experimental data, this analysis cannot explain the physical origin of the multiple time scale relaxation nor determine the orientational diffusion coefficient associated with each time scale.

We have utilized the restricted orientational diffusion models of Wang and Pecora[20] and Lipari and Szabo[21,22] to gain a clearer physical understanding of the origin of multiple time scale orientational relaxation in hydrogen bonded liquids. Within these models, fast orientational diffusion occurs within a restricted cone semi-angle. These models also include a slower, unrestricted orientational relaxation that

follows the initial, restricted relaxation. Using these theoretical models has two primary benefits for understanding orientational relaxation in hydrogen bonding liquids: The cone semi-angle and the diffusion coefficient for restricted relaxation can be directly determined from the anisotropy decay. The cone semi-angle represents a particularly significant observable because it reflects the angular range over which a hydroxyl group can reorient despite being hydrogen bonded to another methanol molecule.

The isotopically pure 26 mol % methanol-d dissolved in CCl$_4$ solution exhibits significantly faster anisotropy decay than the isotopically mixed methanol solution. The faster anisotropy decay results from vibrational excitation transfer.[5,15,16,23–25] Excitation transfer gives rise to a different mechanism for anisotropy decay. Instead of the excitations losing orientational memory as the molecules sample the full range of orientational configurations, the excitations lose orientational memory by transferring to molecules with dipole directions different from those initially excited. For incoherent excitation transfer, the rate of transfer depends strongly on the distance between deuterated hydroxyl stretches, which can be controlled by varying the concentration of methanol-d in solution.[5,15,16,25] While the rate of excitation transfer can also depend on the relative orientations of the transition dipole moments, these effects should be weak for the system being investigated, as will be discussed in Sec. III B.

We have utilized the excitation transfer theory of Huber[26,27] to model the energy transport contribution to the anisotropy decay in the 26 mol % methanol-d solution and to confirm the absence of excitation transfer in the isotopically mixed 0.8 mol % methanol-d 23 mol % methanol-h solution. The ability of this theory to accurately reproduce the experimental anisotropy decay indicates that the excitation transfer and orientational relaxation make additive contributions to the decay rate and that the transfer occurs via an incoherent transition dipole–transition dipole coupling consistent with the Förster energy transfer mechanism.[16]

II. EXPERIMENT

Deuterated methanol-d (Aldrich, 99.5+ atom %), protonated methanol (J. T. Baker, spectroscopic grade), and carbon tetrachloride (Aldrich, HPLC grade) were used as received. Methanol-d has a deuterated hydroxyl group and protonated methyl group. Samples were prepared by weight at 26 mol % for methanol-d and 0.8 mol % methanol-d 23 mol % methanol-h in CCl$_4$. Spectroscopic measurements used home built copper cells with CaF$_2$ windows. Teflon spacers from 50 μm to 1 mm yielded absorbances in the range of 0.5–1.2, respectively, for the δ peak at $\sim$2500 cm^{-1} for both solutions studied. In these sample cells, the solution came in contact only with the CaF$_2$ and Teflon, because metals such as copper catalyze the decomposition of alcohols in CCl$_4$ solution.[28]

The laser system used in these experiments consists of a home built Ti:Sapphire oscillator and regenerative amplifier whose output pumps a three stage optical parametric amplifier (OPA) designed and built in house to produce linearly polarized, tunable mid-infrared light. A bandwidth limiting slit in the stretcher determines the bandwidth of the amplified

seed pulse and provides control of the infrared (IR) pulse duration. The IR output is 1 to 2 μJ per pulse centered at $\sim$2500 cm^{-1}. The IR pulse duration was measured by autocorrelation. The pulses have Gaussian profiles in time and frequency with full width at half maximum (FWHM) of 200 fs in time and 80 cm^{-1} in frequency. The time-bandwidth product was 0.48, which is 1.1 times the transform limit of 0.44 for Gaussian pulses.

The mid-IR pulses are split into pump (90%) and probe (10%) beams that traverse different paths before crossing in the sample. The pump beam is chopped at 500 Hz and directed along a variable path length delay line. A ZnSe Brewster plate polarizer is used to set the probe beam polarization. A small amount of the mid-IR light is split off and used for shot-to-shot normalization. Typically, we collect signal for 900 ms at each time delay in a pump–probe scan and average between 10 and 40 scans. Signal and reference beams impinge on liquid nitrogen cooled MCT detectors whose outputs are processed by gated integrators, divided by an analog processor, and input to a lock-in amplifier. A computer collects the output of the lock-in with an A/D board.

III. RESULTS AND DISCUSSION

The decay of polarization anisotropy in liquids can be determined by measuring the probe polarization dependence of the pump–probe signal.[29,30] By measuring the pump–probe anisotropy decay for both isotopically pure and isotopically mixed solutions of methanol, the rates of vibrational excitation transfer and molecular reorientation can be separately investigated.[5] The experiments were performed on both a 26 mol % methanol-d solution and a 0.8 mol % methanol-d 23 mol % methanol-h in CCl$_4$ solution. In the sample with low methanol-d concentration, vibrational excitation transfer does not occur because of the very large separation between methanol-d molecules, as will be discussed further below. Therefore, any anisotropy decay results from orientational relaxation. The different rates of anisotropy decay between the dilute and concentrated methanol-d samples result from vibrational excitation transfer.

Frequently, the anisotropy decay is determined by measuring the time-dependent signal with the probe pulse parallel to and perpendicular to the pump polarization. Alternatively, the anisotropy decay can be determined by measuring the time-dependent probe intensity with the probe parallel to and rotated to the magic angle, 54.7° from the pump polarization.[30] We have employed the latter approach to measure the anisotropy in these systems.

Excitation of the sample by the linearly polarized pump pulse results in a $\cos^2 \theta$ distribution of vibrationally excited molecules and the corresponding orientational hole in the ground state distribution, where θ represents the angle between the transition dipole moment and the pump polarization vector. For excitation of a hydroxyl stretch, the transition dipole moment will be directed along the OD bond. When the probe pulse has the same linear polarization as the pump pulse, reorientation of the hydroxyl group of methanol-d or excitation hopping,[5,16,25,27,31] which transfers the excitation to another hydroxyl group with a different transition dipole orientation, will result in a diminished sig-

nal. For a probe polarization rotated 54.7° from the polarization of the pump, orientational relaxation is eliminated from the signal.[30] The parallel, $S_\parallel(t)$, and magic angle, $S_{\mathrm{ma}}(t)$, signals can be utilized to determine the time-dependent anisotropy[30]

$$R(t) = \frac{S_\parallel(t) - S_{\mathrm{ma}}(t)}{2S_{\mathrm{ma}}(t)}, \tag{1}$$

which has a theoretical maximum value of 0.4 that decays to zero.

For both samples, the anisotropy also possesses a fast component that decays with a time comparable to the auto-correlation time $\tau_a \approx 180$ fs, with τ_a defined as $\exp(-t^2/\tau_a^2)$. We attribute this fast loss of polarization around $t = 0$ to the decay of the coherent contribution to the pump–probe signal. This assignment is based on the expectation that the excited coherent polarization will decay quickly compared to the time duration of the pulses, and, therefore, it will track the pump–probe instrument response.[32] A similar coherent contribution to the anisotropy for ethanol dissolved in CCl$_4$ has been reported.[23] This fast component contains no information about the rate of the orientational relaxation or excitation transport and will not be addressed further.

As has been shown in great detail previously,[8] the decay of the pump–probe signal caused by vibrational relaxation of the δ methanol-d OD stretch occurs in 500 fs. While excited state decay occurs on a sub-picosecond time scale, orientational relaxation can be observed for tens of picoseconds because vibrational relaxation leads to hydrogen bond dissociation, which produces a persistent pump–probe signal.[8] Because the persistent signal results from the incomplete ground-state recovery of the excited methanol-d molecules, hydrogen bond dissociation produces an orientational hole in the ground state that provides an anisotropic signal for much longer than the 500 fs vibrational lifetime.

The anisotropy decay in the isotopically mixed methanol solution will be discussed first.

A. Restricted orientational diffusion

The parallel and magic angle pump–probe, as well as the anisotropy signals appear in Fig. 2 for the 0.8 mol % methanol-d 23 mol % methanol-h in CCl$_4$. The anisotropy decay in Fig. 2(B) is normalized to unity. The isotopically mixed solution displays a bi-phasic decay, with time constants of 1.7±0.7 and 17±3 ps and amplitudes of 0.18±0.05 and 0.15±0.03, respectively. The sum of the amplitudes for the two decays is 0.33, which does not equal the expected amplitude of 0.4. The observed value of 0.33, obtained by extrapolating the fits to $t = 0$, may indicate that the coherent contribution to the anisotropy signal masks a fast contribution to the anisotropy decay, though the significant error bars on the amplitude values must be recognized. Terahertz spectroscopic studies of orientational relaxation in liquid methanol observe a triexponential orientational relaxation, with the fastest decay occurring on a time scale comparable to or faster than the coherent contribution to the anisotropy signal. Such a fast decay can arise from librational motions. We cannot definitively resolve orientational relaxation occurring
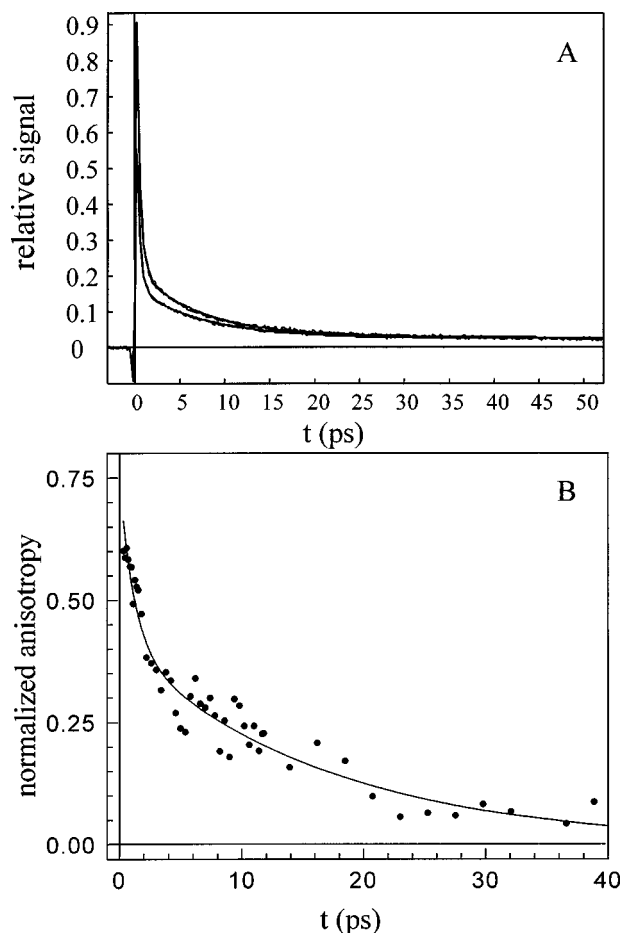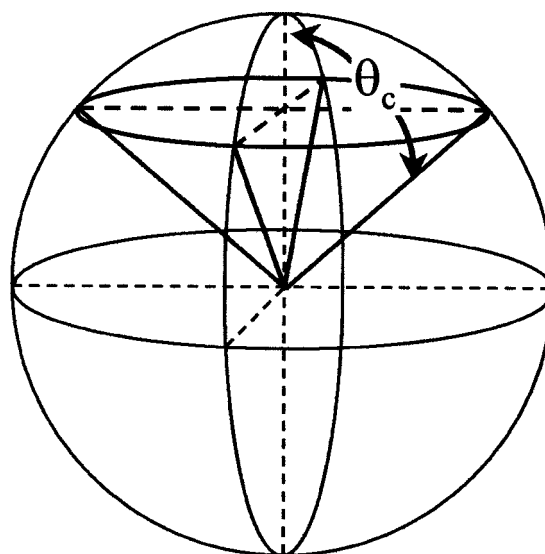
FIG. 3. Schematic depiction of restricted orientational relaxation within a cone of semi-angle θ_c. Orientational diffusion within the cone occurs with diffusion coefficient D_c, while full orientational diffusion on the surface of the sphere occurs with diffusion coefficient D_θ.

FIG. 2. (A) Relative intensities of the pump–probe signal collected with the probe parallel and at the magic angle with respect to the pump polarization. The parallel probe results in the larger amplitude signal. (B) The normalized anisotropy decay for 0.8 mol % methanol-d 23 mol % methanol-h dissolved in CCl_4. The anisotropy decays as a bi-exponential with time constants of 1.7 ± 0.7 and 17 ± 3 ps. Because of the low concentration of methanol-d in the sample, vibrational excitation transfer does not occur, and the depolarization is caused by orientational relaxation.

on the time scale of the coherent signal contribution,[32] so our analysis will focus on the clearly resolved biexponential relaxation.

The analysis utilizes the restricted orientational relaxation models of Wang and Pecora[20] and Lipari and Szabo.[21,22] A schematic depiction of the model appears in Fig. 3. The vector along the transition dipole moment of the methanol-d hydroxyl stretch diffuses within a cone of semi-angle, θ_c, with the diffusion coefficient, D_c. The slower, full diffusion on the surface of a sphere follows the faster, initial orientational relaxation within the cone.

The theoretical description of a time-dependent anisotropy measured with pump–probe spectroscopy involves the calculation of the correlation function,[20–22,30]

$$C_2(t) = \langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle, \tag{2}$$

where $\mathbf{u}$ is a unit vector along the transition dipole moment, $P_2(x) = \frac{1}{2}(3x^2 - 1)$ is the second order Legendre polynomial, and the experimental anisotropy equals[22,30]

$$R(t) = \frac{2}{5} C_2(t). \tag{3}$$

While the exact expression for $C_2(t)$ in the restricted rotational diffusion model involves an infinite sum of exponentials,[20] accurate approximations can be made for cone semi-angles of $<60°$. We have utilized the approximate model of Lipari and Szabo,[21,22] which gives

$$C_2(t) = S^2 \exp(-6D_\theta t) + \{1 - S^2\} \exp(-t[1/\tau_{\text{eff}} + 6D_\theta]). \tag{4}$$

Within this model, $1 - S^2$ represents the fraction of the anisotropy that decays due to orientational diffusion within the cone, τ_{eff} is the characteristic time with which this anisotropy decays, and D_θ is the orientational diffusion coefficient for diffusion on the sphere which results in the full decay of the anisotropy. The sum of the rates, $6D_\theta + \tau_{\text{eff}}^{-1}$, determines the fast relaxation time constant of 1.7 ps. This expression gives $\tau_{\text{eff}} = 1.9$ ps. The cone semi-angle, θ_c, determines the fraction of the anisotropy that does not decay due to diffusion within the cone[21,22]

$$S^2 = \langle P_2(\cos \theta_c) \rangle^2. \tag{5}$$

The fast orientational relaxation, attributed to diffusion within the cone, reduces the anisotropy to 0.15 ± 0.03, or $40 \pm 10\%$ of the total anisotropy. This gives $S^2 = 0.4 \pm 0.1$ and $\theta_c = 45° \pm 5°$. Lipari and Szabo also provide an approximate relationship between τ_{eff} and D_c valid for $\theta_c < 60°$[21]

$$D_c \tau_{\text{eff}} (1 - S^2) = x_0^2 (1 + x_0)^2 \{\ln[(1 + x_0)/2]$$

$$+ (1 - x_0)/2\}/[2(1 - x_0)] + (1 - x_0)$$

$$\times (6 + 8x_0 - x_0^2 - 12x_0^3 - 7x_0^4)/24, \tag{6}$$

where $x_0 = \cos \theta_c$. Using $\theta_c = 45° \pm 5°$ and $\tau_{\text{eff}} = 1.9 \pm 0.7$ ps, the diffusion coefficient for orientational relaxation within the cone is $D_c^{-1} = 13 \pm 5$ ps. The diffusion coefficient for the full, orientational relaxation can be calculated from the 17 ± 3 ps relaxation time with the relation $D_\theta^{-1} = 6\tau = 100 \pm 20$ ps.

Orientational relaxation measurements have been made on methanol and methanol–CCl₄ mixtures using dielectric relaxation[17,19] and steady-state terahertz spectroscopy[18] techniques. The IR pump–probe polarization experiments measure the decay of the molecular dipole anisotropy, which, in the absence of vibrational excitation transfer, measures orientational relaxation through the decay of the directional component of the transition dipole–transition dipole correlation function. In contrast, both dielectric relaxation and steady-state terahertz spectroscopy measure the complex permittivity spectrum of a liquid. The Fourier transformation of a multiexponential Debye model of the anisotropy decay in the time domain results in frequency domain multi-Lorentzian representation of the anisotropy decay. For systems with weak short ranged dipole–dipole correlations, the molecular anisotropy decay measured in the polarization resolved IR pump–probe experiment will occur with the same characteristic time constants as the collective polarization response measured in a dielectric relaxation experiment.[33] By fitting the measured complex permittivity to a sum of Lorentzians with variable widths, the time scales for orientational relaxation can be determined. This data analysis ignores a variety of additional processes that can contribute to the complex permittivity, increasing the value of independent time domain measurements of anisotropy decay.

The times measured with dielectric relaxation and terahertz spectroscopy cannot be compared directly to the orientational relaxation times measured with the IR pump–probe experiments. The correlation function for complete orientation diffusion is $C_l(t) = \exp(-l(l+1)D_\theta t)$. Dielectric relaxation experiments and steady-state terahertz far IR absorption experiments measure the first-order spherical harmonic $C_1(t)$, while the pump–probe experiment measures the second-order spherical harmonics $C_2(t)$. For dielectric relaxation and terahertz spectroscopy, the $l(l+1)$ term in the exponent equals 2, while for the IR pump–probe experiments it equals 6. Therefore, the time constants measured in dielectric relaxation and terahertz experiments need to be divided by 3 for comparison with the IR pump–probe results.

In liquid methanol, analysis of the dielectric relaxation experiments[19] gave three relaxation times of 51.5, 7.09, and 1.12 ps, while terahertz spectroscopy[18] gave three relaxation times of 48, 1.25, and 0.16 ps. Dielectric relaxation measurements performed in solutions of methanol dissolved in CCl₄ also yield three decay times, with the time constants and amplitudes depending upon the methanol concentration.[17] The lowest methanol concentration studied in the dielectric relaxation measurements, 40 mol %, had relaxation times of 155, 23.4, and 2.02 ps.

The slowest relaxation times measured in liquid methanol by both dielectric relaxation and terahertz spectroscopy, when divided by the appropriate factor of 3, strongly resemble the slower relaxation time in the IR pump–probe polarization measurements. This suggests that methanol molecules that accept and donate hydrogen bonds in a 25 mol % solution in CCl₄ undergo full orientation diffusion with an orientational diffusion constant very similar to those found in pure methanol. The similar time constant for orientational

diffusion for the molecular dipole–dipole and the collective dipole–dipole correlation functions also indicate methanol has weak short ranged dipole–dipole correlations.[33] While unexpected, similar results have also been seen for orientational diffusion in water.[34] Interestingly, the 17 ± 3 ps relaxation observed with vibrational pump–probe spectroscopy does not appear to correspond to any of the relaxation processes observed in the dielectric relaxation experiment on the 40 mol % methanol solution.[17] This lack of agreement may reflect the higher molecular specificity of vibrational spectroscopy. While the dielectric relaxation experiment measures simultaneously the response of methanol molecules in all hydrogen bonding states, all types of motions, and motions of any CCl₄ molecules associated with the oligomers, measuring the anisotropy decay with vibrational spectroscopy allows specific hydrogen bonding states to be studied. The orientational dynamics of pure liquid methanol will be overwhelmingly dominated by δ methanol molecules[14] like those excited in our anisotropy measurements, potentially explaining the greater similarity between the results of the present study and dielectric relaxation measurements in liquid methanol[19] than in methanol CCl₄ solutions.[17]

The cone semi-angle provides a particularly critical parameter for understanding structural dynamics in hydrogen bonded liquids. The formation of hydrogen bonds does not allow unrestricted orientational diffusion of the hydroxyl group. The value of θ_c indicates the range of motion permitted for a doubly hydrogen bonded δ hydroxyl stretch. The amplitude of the slowest relaxing component of the polarization response in a dielectric relaxation experiment can provide an estimate of the cone semi-angle. As shown above in Eq. (5), the cone angle can be determined from the fraction of the anisotropy that does not decay due to diffusion within the cone. Dielectric relaxation experiments measure the first-order Legendre polynomial, so

$$S^2 = \langle P_1(\cos\theta_c)\rangle^2, \tag{7}$$

where $P_1(x) = \frac{1}{2}(1+x)$. For methanol, the slowest response represents roughly 90% of the total polarization relaxation.[18,19] Using $S^2 = 0.9$ results in a cone semi-angle of roughly 30° consistent with expectations for moderate strength hydrogen bonds.[35] While clearly less than 45°, this does support the conclusion that hydrogen bonds permit a wide range of angles over which the hydroxyl bond can fluctuate without dissociating a hydrogen bond. Further orientational relaxation would appear to require the dissociation of a hydrogen bond. The diffusion within the cone occurs with a diffusion coefficient roughly an order of magnitude larger than the diffusion coefficient for the full orientational relaxation.

B. Excitation transfer

The time dependence of the anisotropy for the 26 mol % methanol-d differs significantly from that of the isotopically mixed methanol solution. Figure 4 shows the signal for a parallel and a magic angle probe polarization with respect to the pump polarization, as well as the anisotropy. In Fig. 4(A), the rise to the second maximum at ~4 ps is caused by the ~2 ps time scale breaking of hydrogen bonds. This feature
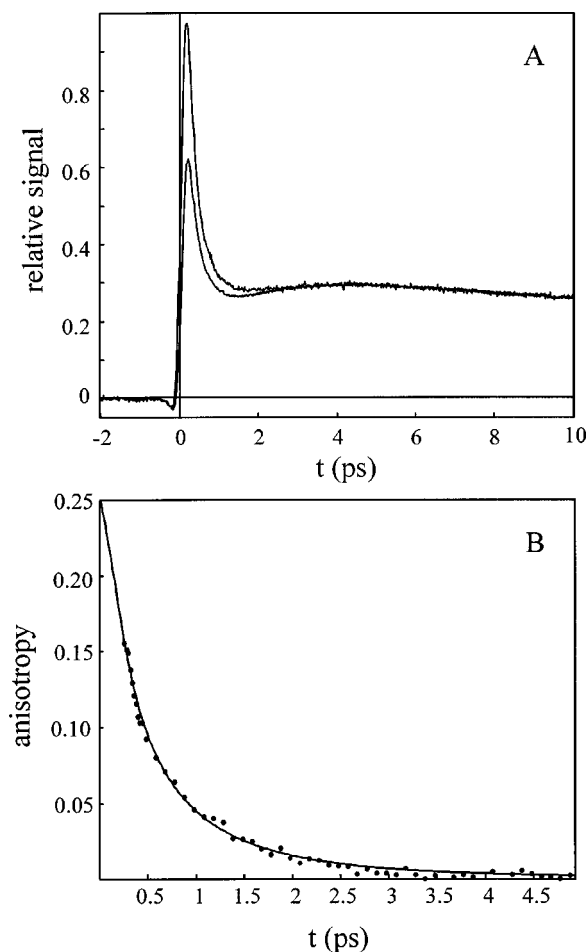
FIG. 4. (A) Relative intensities of pump–probe signal collected with the probe parallel and at the magic angle with respect to the pump polarization. The parallel probe results in the larger amplitude signal. (B) The anisotropy decay for 26 mol % methanol-d dissolved in CCl_4 and the fit to a model that accounts for the combined rates of orientational diffusion and vibrational excitation transfer, as described in Sec. III B.

and its absence in the isotopically mixed sample [see Fig. 2(A)] have been described in detail previously.[8] The increased concentration of deuterated methanol-d in the isotopically pure solution reduces the distances between chromophores and greatly enhances the rate of excitation transfer.[16] For a transition dipole–transition dipole interaction, as in Förster theory, the rate of excitation transfer falls off as $1/r^6$, where r is the intermolecular separation.[16] The anisotropy decay observed in the isotopically pure sample results from a combination of the orientational relaxation observed in the isotopically mixed sample and the additional depolarization caused by excitation transfer, producing a significantly enhanced rate of anisotropy decay.

The complex problem of excitation transfer among many identical molecules randomly distributed in solution has been solved in considerable detail using an infinite order diagrammatic technique.[24] Petersen et al. have shown that a simple time domain expression developed by Huber[26,27] reproduces the infinite order diagrammatic theory result and provides an accurate description of anisotropy decay via excitation transfer.[31]

These theoretical methods describe excitation transfer

for homogeneously broadened transitions. They also assume a random distribution of distances between chromophores and a fixed random distribution of relative transition dipole orientations. The hydroxyl stretch of δ methanol-d does not rigorously meet these criteria. Inhomogeneous broadening clearly plays a role in determining the width of the δ OD stretch transition.[8,36] Inhomogeneous broadening can lead to dispersive excitation transfer even in solution at room temperature.[37] For the case of δ OD vibrations, dispersive transfer should be of limited significance because the thermally accessible range of energies, $k_B T \approx 200$ cm^{-1}, exceeds the ~ 150 cm^{-1} width of the δ hydroxyl stretch absorption.

The time-dependent orientational relaxation will be accounted for using the results presented in Sec. III A. However, the rate of excitation transfer depends on the relative angles between the transition dipoles. The dependence is not strong as long as a broad distribution of angles is sampled. The transition dipole–transition dipole intermolecular interaction responsible for excitation transfer is characterized by the Förster radius, R_0.[15,16] R_0 is defined as the distance of separation between two chromophores at which the probability of excitation transfer is equal to the probability of excited-state relaxation to the ground state. If orientational relaxation is very fast compared to excitation transfer, then the angle averaged transfer rate is appropriate, that is, there is no specific angular dependence. If the chromophores are static, then the solution to the transport master equation must be averaged over angles. For a random distribution of angles, the average over angles results in the multiplication of the angle averaged R_0 by a factor of 0.946; the angle average does not change the functional form of the decay.[25] The comparison of the two cases demonstrates that the influence of the angular factors on R_0 is not large. Because the rate of transfer depends on R_0^6, the rate of excitation transfer is reduced by 28% for static randomly oriented dipoles compared to the angle averaged transfer rate. In the problem being considered here, we do not have a random distribution of angles, but the cone semi-angle is large (see above). For two hydroxyls, there will be a broad distribution of relative angles. In addition, the system is between the dynamic and static limits. Therefore, the influence of the distribution of angles on the calculation should be small, and the functional form of the decay is not expected to be modified substantially.[25]

For the calculation of excitation transfer induced depolarization, the key function is $G^s(t)$, the probability that the initially excited chromophore is still excited at time t.[24,25] $G^s(t)$ has contributions from excitations that have never left the initially excited chromophore and from excitations that have left and returned. The most thorough treatment of the problem includes an infinite number of randomly distributed chromophores with an infinite number of pathways for the excitation to leave and return to the initially excited chromophore.[24] While the high methanol concentration will make interoligomer transfer possible and reduce the correlations in the methanol–methanol distances, the isotopically pure methanol solution will still have a nonrandom distribution of chromophores. Excitation transfer with a nonrandom distribution of a finite number of chromophores has been

treated in the context of excitation transfer on polymer chains.[31,38] The nonrandom distribution does change the functional form of the decay to some extent.[31] Despite these limitations, treating the rate of anisotropy decay in the 26 mol % methanol-d solution as a sum of the rate of orientational diffusion found in the isotopically mixed methanol solution and the rate of excitation transfer for randomly distributed chromophores reproduces the data within experimental accuracy.

We utilize the excitation transfer theory of Huber to describe our experimental data.[26,27] The ensemble averaged probability that a chromophore initially excited by the pump pulse will still be excited at time t, $G^s(t)$, provides the quantity of interest

$$G^s(t) = \exp\left[-\frac{4\pi^{3/2}}{3} 2^{3/5} c R_0^3 \frac{t^{1/2}}{\tau_r^{1/2}} \right], \tag{8}$$

where c is the concentration, R_0 is the Förster radius, and τ_r is the δ hydroxyl stretch lifetime. We modeled the anisotropy decay in the 26 mol % methanol-d solution, $R_p(t)$, as the product of isotopically mixed methanol relaxation, $R_m(t)$, and $G^s(t)$

$$R_p(t) = R_m(t) G^s(t), \tag{9}$$

with $c = 24.7$ M, the concentration of hydroxyl stretches in liquid methanol at room temperature, and $\tau_r = 500$ fs as measured experimentally.[8,39] We use the liquid methanol concentration since methanol forms oligomers in CCl_4 with similar short-range structure to that found in liquid methanol.[12] The best fit of the model to the data is shown in Fig. 4, and it gives an $R_0 = 2.03 \pm 0.04$ Å. The agreement between the calculation and the data is very good. The calculated curve is the product of $R_m(t)$, a biexponential function, and $G^s(t)$, an exponential function of $t^{-1/2}$, where the only adjustable parameter is R_0. Varying R_0 does not change the functional form of the curve. While R_0 can be fit with small error bars, the value may have systematic errors because of assumptions made in applying the theory for excitation transfer between randomly distributed chromophores to excitation transfer in methanol oligomers.

Given the square root dependence of the time in the exponent for $G^s(t)$,[26,27] the rate of excitation transfer decreases quadratically with decreasing concentration. One in thirty methanol molecules has a deuterated hydroxyl stretch in the isotopically dilute methanol-d solution. The reduction in concentration makes the rate of excitation transfer roughly three orders of magnitude slower than that observed in the isotopically pure methanol-d solution, validating the assumption that only orientational relaxation contributes to the anisotropy decay in the isotopically dilute methanol-d solution.

Hydroxyl stretch excitation transfer in hydrogen bonded ethanol and water has been investigated previously.[5,23] As a result of these experiments, Bakker concluded that excitation transfer provides an important route for energy relaxation in hydrogen bonded systems. The results of the present work bring this conclusion into doubt. In polarization resolved studies of δ hydroxyl stretches in isotopically pure ethanol-h dissolved in CCl_4, Woutersen et al. found the anisotropy to decay with a time constant $\tau \leqslant 300$ fs to a delay time-

independent offset. They attributed the fast anisotropy relaxation to vibrational excitation transfer. These results cannot be reconciled with our measurements of δ hydroxyl stretches in isotopically pure methanol-d, where the time scale for excitation transfer can be clearly resolved and the anisotropy does decay to zero, as shown in Fig. 4. While small deviations between methanol and ethanol should be expected, the rate of excitation transfer in methanol should be larger, not smaller, given that methanol has a 50% higher density of hydroxyl groups than ethanol. In vibrational excitation transfer studies of the protonated hydroxyl stretch in partially protonated heavy water and pure water,[5] Bakker observed an OH concentration dependent anisotropy decay for two concentrations of OH in isotopically mixed samples. They fit their data to a theory with the same functional form as Eq. (7) and obtain a Förster radius of $R_0 = 2.1$ Å.[5] The data analysis, however, employed an earlier theoretical description of excitation transfer[40] that differs from the Huber theory by a factor of $2^{3/5}$ in the exponential term.[26,27] Reanalyzing the isotopically mixed water data with the accurate Huber equation gives $R_0 = 1.8$ Å. The comparative rates of excitation transfer and excited-state decay will depend upon the Förster radius to the sixth power.[15,16] Using a value of $R_0 = 1.8$ Å, and an intermolecular separation of 2.8 Å, the rate of vibrational decay will exceed the rate of excitation transfer by an order of magnitude. Based on this analysis, Förster type excitation transfer in liquid water will not represent a significant energy transfer mechanism. The inability of excitation transfer theory to describe the observed rate of anisotropy decay in pure water using the R_0 value obtained from the isotopically mixed water system[5] would appear to indicate that a new mechanism for anisotropy decay exists in pure water. The existence of an additional transfer mechanism in pure water should not be viewed as surprising given the possibility for intramolecular excitation transfer. In the isotopically mixed samples few water molecules will have two protonated hydroxyl stretches, making excitation transfer predominantly intermolecular. In pure water all molecules possess two protonated hydroxyl stretch modes, and excitation transfer can be intramolecular as well as intermolecular.

The fast excitation transfer we observe for 26 mol % methanol-d in CCl_4 clearly demonstrates that hydroxyl stretch vibrational excitation transfer occurs for molecules other than water. In both methanol and water the rate of excitation transfer is slower than the rate of vibrational relaxation. Interestingly, even for the isotopically pure methanol-d clusters in high concentration methanol solutions, the rate of excitation transfer can be effectively described with incoherent excitation transfer theory developed for a random distribution of chromophores.

IV. CLOSING REMARKS

The IR pump–probe vibrational anisotropy decay was measured in an isotopically mixed 0.8 mol % methanol-d 23 mol % methanol-h dissolved in CCl_4 solution and in an isotopically pure 26 mol % methanol-d dissolved in CCl_4 solution. The anisotropy decay results from orientational diffu-

sion in the isotopically mixed methanol solutions and a combination of orientational diffusion and excitation transfer in the isotopically pure methanol solution.

The isotopically dilute solution of methanol-d has a biexponential anisotropy decay with time constants of 1.7 ± 0.7 and 17 ± 3 ps and amplitudes of 0.18 ± 0.05 and 0.15 ± 0.03, respectively. The total anisotropy amplitude does not equal the theoretical maximum value of 0.4, which may indicate that a very fast orientational relaxation occurs on a time scale comparable to or shorter than the pulse duration. Hindered rotations, which will not be diffusive on the 100 fs time scale, could be the source of this very fast process. However, the maximum value of 0.4 is almost within the error bars of the measurements.

We have analyzed the biexponential orientational relaxation with the restricted orientational diffusion theory of Wang and Pecora[20] and Lipari and Szabo.[21,22] Within this model, the 1.7 ± 0.7 ps anisotropy decay results from diffusion within a cone of semi-angle $\theta_c = 45° \pm 5°$ with a diffusion coefficient of $D_c^{-1} = 13 \pm 5$ ps. The 17 ± 3 ps relaxation corresponds to the full orientational diffusion. The orientational diffusion coefficient for the full orientational relaxation is $D_\theta^{-1} = 100 \pm 20$ ps, consistent with the diffusion constants measured in pure methanol with dielectric relaxation[19] and terahertz spectroscopy[18] experiments. The large value of the cone semi-angle indicates the hydroxyl stretch samples a substantial range of orientations relatively unhindered by the presence of hydrogen bonds. The full orientational diffusion occurs with an order of magnitude smaller diffusion coefficient than that for orientational relaxation within the cone.

The dynamics of vibrational excitation transfer have also been studied in isotopically pure 26 mol % methanol-d dissolved in CCl_4. These dynamics have been effectively modeled with the excitation transfer theory of Huber for transfer between randomly distributed and oriented transition dipoles in solution.[26,27] These results demonstrate that vibrational excitation transfer occurs in methanol, as has been seen for water.[5]

The rate of orientational relaxation in dipolar liquids determines the rate of dielectric relaxation and solvation,[2,3] which influences reaction dynamics in dipolar solvents. These effects have been widely investigated in theoretical and experimental studies of electron transfer reactions.[1,41,42] For a reaction involving a redistribution of solute charges in a dipolar solvent, the polarization of the solvent must respond to the time-dependent redistribution of solute charges as the reactants make a transition to products. This time-dependent polarization, or alternatively the dielectric solvation dynamics, will exert a drag on the redistribution of charges occurring during the reaction, often termed dielectric friction. Reactions with large friction and small reaction barriers can have solvation dynamics limited reaction rates.[43,44] The presence of a large amplitude orientational relaxation occurring significantly faster than that of the Debye–Stokes–Einstein orientational diffusion time constant,[45] significantly reduces the dielectric friction and effectively increases the rate of solvation controlled electron transfer reactions by decreasing the time scale for motion along the reaction coordinate in outer sphere electron transfer reactions.[41,44]

While the presence of dielectric relaxation and solvation times faster than the Debye orientational diffusion time constant have been observed previously in methanol with alternative experimental techniques,[3,18,19,46] time resolved vibrational spectroscopy has many useful advantages over electronic spectroscopy and dielectric relaxation measurements that may provide a more detailed molecular scale understanding of solvation dynamics in solution. The Ångstrom size of the hydroxyl stretch probe of solvation dynamics will make the technique sensitive to short-range molecular scale events that long wavelength spectroscopies, such as dielectric relaxation measurements, cannot observe. The technique also has the advantage of being able to monitor the short-range solvation dynamics without distorting the short-range structure in the liquid, something that cannot be achieved in solvation dynamics studies that employ large solute chromophores as the probe of solvation dynamics. It is possible that time resolved vibrational spectroscopy will be able to resolve the relative importance of short-range molecular and long range collective motions in the solvation dynamics of dipolar solvents.

ACKNOWLEDGMENTS

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